

Low-Temperature Performance of Lithium-Ion Batteries

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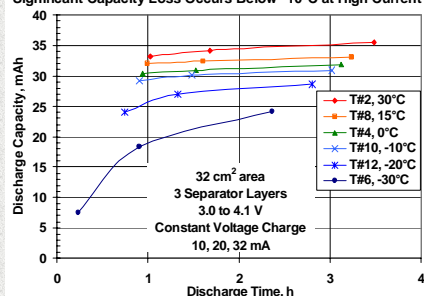
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Introduction

Lithium-ion batteries are rapidly becoming the battery of choice for portable electronic devices such as laptops, cell phones, and cameras. They have also received much interest for use in hybrid electric vehicles (HEVs), which require high power. While lithium-ion batteries have abundant power at room temperature, their power is poor at the low temperatures that HEVs will experience in normal use. The goal of this work is to determine the reason for this power loss using *in situ* micro reference electrodes coupled with electrochemical performance characterization over a wide temperature range of 40°C to -30°C.

Significant Capacity Loss Occurs Below -10°C at High Current



Challenges

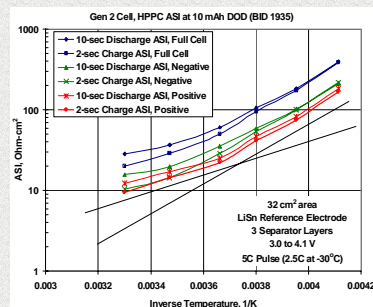
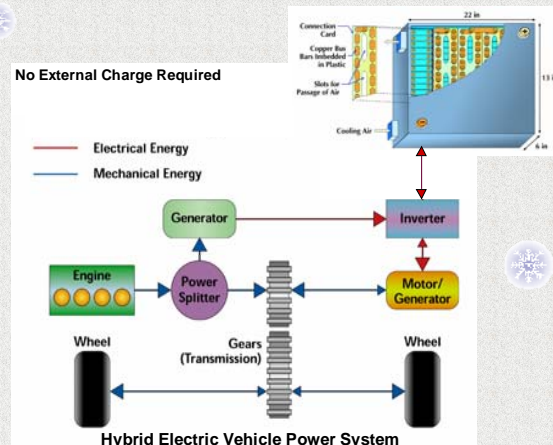
Many researchers have attempted to improve the low-temperature performance of lithium-ion batteries by developing electrolytes with high ionic conductivities at low temperature. However, when these electrolytes were used in actual full cells, there was only a marginal improvement in performance. Clearly, another mechanism was at work. An *in situ* technique was needed that could elucidate the reason for the poor low-temperature performance.

Argonne's Approach

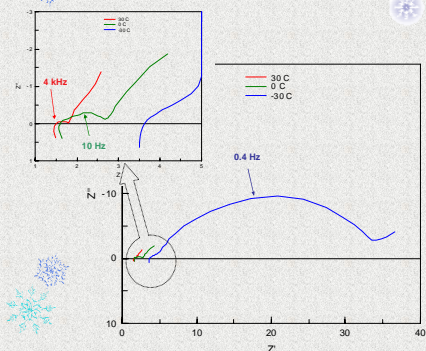
We decided to investigate the electrochemical processes taking place on the negative and positive electrodes using *in situ* micro reference electrodes (RE) that we developed earlier in our advanced battery work. The micro RE consists of a 1-μm-thick tin coating on a 25-μm-diameter copper wire that is coated with an insulating polyurethane coating. A 1-cm length of the polyurethane coating is removed prior to use to expose the tin surface. A cell is assembled with the micro-RE placed between two layers of separator in the cell and then charged with lithium from either electrode.

Constant current cycling and pulse-power tests are performed on lithium-ion cells with varying compositions at decrements of 10 to 15°C from 45°C down to -30°C. Electrochemical impedance spectroscopy (EIS) studies are performed on these cells over a frequency range of 60 kHz to 2 mHz.

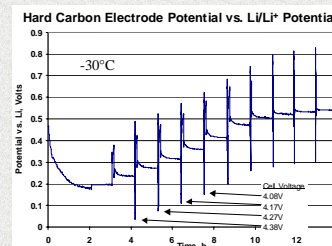
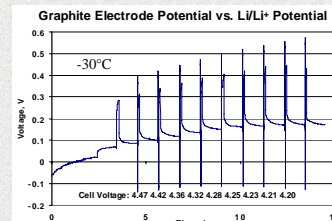
The concern also exists that lithium metal might plate on the negative electrode during high current charge pulses, a condition that would result in excessive capacity loss. Reference electrodes are ideally suited to explore this possibility as well.



Pulse power impedance increases abruptly at -10°C due to almost equal contributions from the negative (graphite) and positive (LiNi_{0.8}Co_{0.15}Al_{0.05}O₂) electrodes.



Electrochemical impedance spectroscopy data for a lithium-ion cell indicates a large increase in interfacial impedance at low temperature.



The potential of the graphite negative electrode does dip below lithium potentials not only during charge pulses, but also under normal charging if the cell cutoff voltage is not reduced from its room temperature setting of 4.1 V. Cells based on hard carbon as the negative electrode are much less likely to deposit lithium because hard carbon operates at potentials 200 to 800 mV above lithium potential, whereas graphite has a long voltage plateau only 100 mV above lithium potential.

Conclusions

In situ micro reference electrodes are a valuable tool to elucidate the electrochemical processes that take place in a lithium-ion cell, and are particularly well adapted for low-temperature studies. The most surprising finding from this work was that the impedance rise at low temperature was due to nearly equal contributions from the positive and negative electrodes. The high-frequency impedance data indicated that the electrolyte conductivity does increase as the temperature is lowered, as expected, but is not the dominant cause of the impedance rise. The main rise in impedance occurs in the mid-frequency range of the spectrum. Processes that occur in this frequency range are generally interfacial in nature. This means that the responsible phenomenon is independent of the active material and is most likely an electrolyte-interface effect.